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## COMPLETE SPECIFICATION

## Print Paste

We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company, of Ludwigshafen/Rhein, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to new print pastes for textile printing comprising water-in-oil emulsions containing pigment and binder, and to a process for preparing the print pastes.

Unbodied print pastes (i.e. print pastes which contain no thickeners e.g. alginates) which consist essentially of an external organic phase and an internal aqueous phase (water-in-oil emulsions) with pigments and cross-linkable film-forming binders have long been known.

The properties of such pastes in use and consequently the quality of the prints produced with these pastes depend not only on the type of components, for example binder, but also to a great extent on how the individual components are distributed to the internal and external liquid phases. Accordingly a number of different systems is known which—expressed somewhat simply—seek to solve the problem of reconciling to each other two contrary properties of such emulsions to a harmonious optimum. On the one hand the greatest possible stability is required of the emulsion until it has been applied so that, for example, no separation into the components takes place.

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This is achieved as a rule by keeping the chemical affinity of the two liquid phases for each other as low as possible, for example by avoiding the use of components which remain in both phases. On the other hand, however, the components of the emulsion should be as compatible with each other as possible.

The exacting requirements as to the quality of the products and their application cannot however be fulfilled satisfactorily by the prior art systems, as made clear by the following survey of the state of the art:

In the textile print pastes described in British Patent Specification No. 523,090 the pigment and heat-curable aminoplast or alkyd resin as the binder are present in the outer organic phase. Prints produced therewith have however only moderate fastness to rubbing and washing.

Furthermore print pastes are known from British Patent Specification No. 887,637 which are based on water-in-oil emulsions containing heat-curable condensation resins in the outer organic phase and a non-crosslinkable polymer in the inner aqueous phase. Similar products are known from U.S. Patent Specification No. 2,691,005.

Multiphase systems are recommended in British Patent Specification No. 561,641. These systems are however very susceptible to separation into their components which means that once a recipe has been adopted it must not be modified by varying the relative proportions of the components in order to produce variations in the color strength or viscosity.

According to British Patent Specification No. 877,369 dispersed crosslinkable copolymers are used as binders in the inner aqueous phase while the external phase does not contain any binder.

The said systems however have quite generally either disadvantages in processing (they are very susceptible to a change in the recipe) or the prints produced therewith are unsatisfactory.

We have now found that print pastes comprising water-in-oil emulsions, crosslinkable film-forming binders and pigments have excellent properties in use and impart to prints produced therewith outstanding mechanical properties when they have substantially the following constitution:

(I) 1 part by weight of an inner aqueous phase which contains:—

(a) 0.1 to 10% (percentages are by weight throughout this specification) of a pigment dispersed therein;

(b) 1 to 20% of a water-insoluble film-forming cross-linkable polymer; and

(c) 0.1 to 10% of one or more emulsifiers required for emulsification of (a) and (b); the percentages of (a), (b) and (c) relating to the amount of (I); and

(II) 0.1 to 1 part by weight of an outer organic phase which essentially contains, in addition to an organic liquid:—

(d) 0.5 to 30% of a binder soluble in this phase; and

(e) 2 to 20% of an emulsifier for the dispersion of (I) in (II), the percentages of (d) and (e) relating to the amount of (II).

The upper limits of concentration for (d) and (e) apply where the amount of the outer organic phase (II) is at the lower limit. The converse is true for the lower limits of concentration of (d) and (e).

We have also found that the print pastes according to this invention are advantageously obtained by first intimately mixing the components (d) and (e) with the solvent of the organic phase (II) and then stirring the aqueous dispersion of (I) containing (a), (b) and (c) by means of an impeller into (II) to produce the emulsion thickening.

Inorganic and organic pigments of all types, for example titanium dioxide, the various iron oxides, carbon black, and azo dyes, anthraquinone dyes and phthalocyanine dyes which are insoluble in water and in the organic phase (II) and which are preferably used in the form of aqueous pastes containing emulsifier are suitable as the pigments (a).

Particularly suitable film-forming cross-linkable polymers (b) are those obtainable from:—

(i) 1 to 10% of N-methylolacrylamide or N-methylolmethacrylamide or the  $C_1-C_4$  alkyl ethers of these methylol compounds or monomers containing halohydrin groups, for example 2-hydroxy-3-chloropropyl acrylate and

(ii) 99 to 90% of conventional comonomers for the production of such binders, such as butadiene, styrene, acrylic acid, methacrylic acid, acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, esters of acrylic acid, methacrylic acid and vinyl esters having up to twelve carbon atoms, vinyl chloride and N-vinylpyrrolidone. Since the chemical composition of the polymers (b) is immaterial provided they are water-insoluble, film-forming and crosslinkable, the list above contains only the comonomers most widely used in industry, and it is not intended to imply that less common comonomers are not suitable.

Polymers (b) having the following tabulated compositions are given by way of example:—

	Composition in %						
butadiene							60
styrene			24				
vinyl chloride		15					40
vinyl acetate				40			
acrylic acid				2		1	
methyl acrylate					10		
ethyl acrylate			6				
butyl acrylate	72	60	65	54	66	60	55
2-hydroxy-3-chloropropyl acrylate						10	
methyl methacrylate						14	
methacrylamide							5
N-methylolacrylamide			5	4			
N-methylolmethacrylamide	4	5			4		5
acrylonitrile	24	20			20	15	35

These and other polymers are obtainable by known methods.

- 5 Anionic and nonionic surfactants are particularly suitable as emulsifiers (c) for the aqueous phase (I). Among the many suitable compounds, alkenoxylated fatty alcohols and phenols and also alkyl sulfates, alkyl sulfonates, aryl sulfates and aryl sulfonates may be given as examples.

- 10 These emulsifiers may in some cases already be present in the aqueous dispersion of (b), stemming from the emulsion polymerisation, so that the dispersion has only to be mixed with the pigment dispersion. It is however also possible to stir the dry pigment or pigment paste into the polymer dispersion using appropriate amounts of emulsifier.

- 20 Suitable organic liquids for the outer phase (II) are those which have been conventionally used for the production of water-in-oil emulsions, preferably hydrocarbons and mixtures of hydrocarbons having boiling point ranges of from 100° to 300°C, and also chlorinated hydrocarbons as the sole solvent or together with the abovementioned solvents. For example mixtures of 60 to 90% of heavy naphtha (boiling range 100° to 200°C) and 30 10 to 40% of toluene and xylene have proved to be very suitable.

The soluble binders (d) in phase (II) may be particularly those which themselves cross-link or crosslink with the polymers (b) of the aqueous phase (I). Macromolecular substances which are not crosslinkable, including particularly thermoplastic polymers, are however also suitable.

Binders which are cross-linkable polymers which are soluble in the organic phase (II) are preferred. Thus these binders (d) may be built up from the same classes of monomers as the polymers (b) described in detail above. Specifically, reference is made to the statements as to the advantageous composition of the polymers (b) and the tabulated examples thereof. Since however the polymers (b) are advantageously prepared by emulsion polymerization in aqueous medium, but the polymers (d), where possible, are prepared by solution polymerization in the solvent of phase (II), the polymers (b) and (d) are in general not identical.

Both polymers (b) and (d) should in general be characterized by K values of from 20 to 100 measured as 1% solutions in dimethylformamide at 25°C.

Besides the above-mentioned polymers other crosslinkable binders soluble in the organic phase II can be used as binder (d) e.g. urea-

formaldehyde resins and epoxy resins (the latter example with polymers (b) that cross-link under alkaline conditions and their precondensates. These resins and their precondensates may provide all or part of the binder (d).

Suitable emulsifiers (e) which are added to phase (II) prior to the production of the emulsion thickening, are the substances conventionally used for this purpose, for example fatty acid amides, such as oleic acid monoethanolamide and oleic acid diethanolamide.

Besides the essential constituents in phases (I) and (II) of the print pastes according to this invention defined above, the print pastes may contain, especially in the aqueous phase, known assistants, for example acid or basic crosslinking catalysts, such as ammonium chloride or organic amino compounds, hydro-tropic substances, such as glycol, glycerol or urea, plasticizers, such as diisooctyl phthalate, and thickeners, such as alginates, film-forming thermoplastic polymers or crosslinking components, such as aminoplast precondensates. Whether the assistants in a given case are compatible with the other components can be determined without difficulty by preliminary test.

All conventional methods may be used for preparing the emulsion thickenings according to this invention, those already described above having proved to be particularly suitable.

The print pastes thus obtained may be used in the same way as prior art emulsion thickenings which contain pigments and crosslinkable film-forming binders. They may accordingly be used for direct printing and also for special methods, such as matt white, matt color, graphite and bronze printing and (with the use of the necessary agents) for reserve or discharge printing, and for fibrous materials of all types, including woven fabrics, knitted fabrics and non-woven fabrics of cotton, rayon staple fiber, wool, silk, cellulose acetate, viscose, polyamide, polyester and polyacrylonitrile fibers and also asbestos fibers and glass fibers.

The prints may be fixed by conventional methods, the temperature and the duration of the heat treatment depending in known manner on the type of crosslinkable binder component and the susceptibility of the fibrous material. As a rule the system is chosen so that vegetable fibers are exposed for from two to ten minutes to temperatures of from 80° to 140°C, while with polyamide and polyester fibres higher temperatures and consequently shorter fixing times may be used.

Print pastes according to this invention have excellent properties in use. They are for example very stable and substantially insensitive to variations in the formulations by subsequent addition of one or other component. It is also of great advantage that prints which are obtained with these pastes have outstand-

ing fastness, for example fastness to washing. The following Examples will further illustrate the invention. The percentages are by weight.

#### EXAMPLE 1

A dispersion of:—  
10 parts of 35% aqueous pigment paste of chlorinated copper phthalocyanine,  
10 parts of a 45% aqueous dispersion of a copolymer of 66% of butyl acrylate, 20% of acrylonitrile, 10% of methyl methacrylate and 4% of N-methylolacrylamide,  
about 2 parts of emulsifiers contained in the said dispersion, 3 parts of a 50% aqueous ammonium nitrate solution and 56 parts of water,  
is stirred into an organic solution of:—  
5 parts of a 50% solution of a copolymer of 51% of styrene, 45% of 2-ethylhexyl acrylate and 4% of the butyl ether of N-methylol methacrylamide in a mixture of kerosene and benzene;  
2 parts of oleic acid diethanolamide and 12 parts of a mixture of 60% of white spirit and 40% of toluene, by means of an impeller to form a water-in-oil emulsion thickening.

A union fabric of cotton and polyester is printed with this print paste by roller printing, the fabric then being dried and the print fixed by heating for five minutes with hot air at 140°C.

The print obtained has excellent wet fastness.

#### EXAMPLE 2

A dispersion of:—  
5 parts of a 30% aqueous pigment paste of the azo dye from 3-amino-4-methoxybenzene sulfonic acid diethylamide and 2,3-hydroxynaphthoic acid - 3' - chloro-4',6' - dimethoxyanilide,  
12 parts of a 40% aqueous dispersion of a copolymer of 59% of butyl acrylate, 15% of methyl methacrylate, 15% of acrylonitrile, 1% of acrylic acid and 10% of 2-hydroxy-3-chloropropyl acrylate,  
about 3 parts of an emulsifier mixture and 62 parts of water

is processed as in Example 1 with an organic solution of:—

3 parts of pentaerythritol glycidol ether and 15 parts of xylene  
to form an emulsion thickening with which a rayon staple fiber cloth is printed by screen printing. The cloth is dried and the print is fixed by steaming for ten minutes at about 102° to 103°C. A print having outstanding fastness is obtained.

#### EXAMPLE 3

A dispersion of:—  
6 parts of a 30% aqueous pigment paste of monobromoisodibenzanthrone,

- 15 parts of a 50% aqueous dispersion of a copolymer of 54% of butyl acrylate, 44% of vinyl acetate and 2% of acrylic acid, about 2 parts of an emulsifier mixture, 2 parts of a 75% aqueous solution of an aminoplast precondensate, 3 parts of a 33% aqueous solution of diammonium phosphate and 56 parts water, is processed as in Example 1 with an organic solution of:—
- 3 parts of a 50% toluene solution of a copolymer of 50% of butyl acrylate and 50% of vinyl acetate, 3 parts of oleic acid monoethanolamide and 10 parts of light naphtha to form an emulsion thickening with which polyester cloth is printed by roller printing. The cloth is dried and the print is fixed for one minute at 180°C with hot air. A print is obtained having outstanding fastness properties.

## EXAMPLE 4

- A dispersion of:—
- 10 parts of a 50% aqueous titanium dioxide suspension, 10 parts of a 45% aqueous dispersion of a copolymer of 55% of butyl acrylate, 40% of vinyl chloride and 5% of methacrylamide, about 2.5 parts of an emulsifier mixture, 3 parts of a 25% aqueous ammonium chloride solution and 59.5 parts of water is processed as in Example 1 with an organic solution of:—
- 3 parts of a 50% gasoline solution of a precondensate of propylenurea and formaldehyde, 2 parts of dodecylhydroxyethyl sulfide and 10 parts of a mixture of 60% of white spirit and 40% of carbon tetrachloride to form an emulsion thickening with which cellulose acetate cloth is printed by roller printing. The cloth is dried and the print is fixed by hot air at 120°C for ten minutes. A matt white print is obtained having good fastness properties.

## EXAMPLE 5

- A dispersion of:—
- 8 parts of a 50% aqueous titanium dioxide suspension, 0.5 part of a 30% aqueous copper phthalocyanine pigment paste, 15 parts of a 40% aqueous dispersion of a copolymer of 60% of butadiene, 35% of acrylonitrile and 5% of N-methoxymethacrylamide, about 2 parts of an emulsifier mixture, 3 parts of a 50% ammonium thiocyanate solution and 50 parts of water is processed as in Example 1 with an organic solution of:—

- 4 parts of a 50% solution in a mixture of kerosene and benzene of a copolymer of 14% of styrene, 80% of isobutyl acrylate and 6% of N-ethoxymethacrylamide, 2.5 parts of oleic acid monoethanolamide and 15 parts of a mixture of 60% of white spirit and 40% of toluene to form an emulsion thickening with which a viscose cloth is printed by roller printing. The cloth is dried and the print is fixed with hot air for five minutes at 140°C. A matt colour print having excellent fastness properties is obtained.

## EXAMPLE 6

- A dispersion of:—
- 6 parts of a 30% aqueous copper phthalocyanine paste, 10 parts of a 45% aqueous dispersion of a copolymer of 50% of butyl acrylate, 46% of styrene and 4% of N-methylolmethacrylamide, about 2 parts of an emulsifier mixture, 4 parts of tartaric acid and 1 part of water is processed as in Example 1 with an organic solution of:—
- 3 parts of glycerol diglycidyl ether, 2 parts of oleic acid diethanolamide and 12 parts of a mixture of 60% of white spirit and 40% of toluene to form an emulsion thickening with which a cotton cloth is printed. The cloth is dried and the print is fixed by heating at 140°C with hot air for five minutes. A print is obtained which does not lose its high quality upon subsequent reserve dyeing. Reserve dyeing is carried out with a liquor containing, in 1 liter of water, 25 g of a reactive azo dye (diazotised sulfuric acid ester of  $\beta$ -hydroxypropionic acid-*m*-aminoanilide  $\rightarrow$  1,4-naphtholsulfonic acid), 50 g of urea, 10 g of sodium carbonate and 2 g of sodium alginate. The printed cotton cloth is padded with this liquor and then dried and steamed for five minutes at 103°C to fix the dyeing. The reserve print obtained has very good fastness properties.

## WHAT WE CLAIM IS:—

1. A print paste comprising a water-in-oil emulsion, a crosslinkable film-forming binder and a pigment, which contains:—
  - (I) 1 part by weight of an inner aqueous phase containing
    - (a) 0.1 to 10% by weight of a pigment dispersed therein;
    - (b) 1 to 20% by weight of a water-insoluble film-forming crosslinkable polymer; and
    - (c) 0.1 to 10% of one or more emulsifiers required for the emulsification of (a) and (b), the percentages for (a), (b) and (c) relating to the amount of (I), and

- (II) 0.1 to 1 part by weight of an outer organic phase which essentially contains in addition to an organic liquid:—
- 5 (d) 0.5 to 30% of a binder soluble in this phase; and
- (e) 2 to 20% of an emulsifier for dispersing (I) in (II), the percentages for (d) and (e) relating to the amount of (II).
- 10 2. A print paste as claimed in claim 1 wherein the component (d) of phase (II) is built up from the same classes of monomers as those of the component (b) of phase (I).
- 15 3. Print pastes as claimed in claim 1 and described in any of the foregoing Examples.
4. A process for the production of a print paste as claimed in any of claims 1 to 3 wherein components (d) and (e) are first intimately mixed with the solvent of the organic phase (II) and then the dispersion (I) containing (a), (b) and (c) is stirred into phase (II) by means of an impeller to produce a water-in-oil emulsion thickening.
5. A process as claimed in claim 4 carried out substantially as described in any of the foregoing Examples.

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